PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60607/WO	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/GB2004/002854	International filing date *(day/month/year)* 02.07.2004	Priority date *(day/month/year)* 18.07.2003
International Patent Classification (IPC) or national classification and IPC C09B47/06, C09B47/26, C09B67/22, C09D11/00		
Applicant AVECIA LIMITED et al		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 4 sheets, as follows:
      ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☒ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (Indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☒	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
21.02.2005	15.12.2005
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Ketterer, M Telephone No. +31 70 340-3645

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/GB2004/002854

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

   Description, Pages

   1-19 as originally filed

   Claims, Numbers

   1-17 received on 18.03.2005 with letter of 16.03.2005

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☒ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☒ the claims, Nos. 6-17
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

   * *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-17
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-17
Industrial applicability (IA)	Yes:	Claims	1-17
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

V. Reference is made to the following documents:

D1: US -A- 2001011396
D2: WO -A- 01/66647
D3: WO -A- 01/66648
D4: WO -A- 03/068866
D5: WO -A-98/49239
D6: WO -A- 98/49240

V.1. Rule 70.2(c); Article 19(2) PCT:
The amendments handed in with letter from 16th March 2005 are not allowable with respect to Artikel 19(2) PCT. New claim 6 defines indices ranges from 0.5 - 3.0 for x,y and z. In the original application these ranges have been defined for the substituents R1,R2,R3,R4,R5 and L (please see page 4, lines 26-30). In new claim 6 these values for x,y and z refer also back to the formulas (2) and (3) of claims 2 and 4, in which also the substituents R6,R7,R8,R9 are defined. The application original filed does not explicitly disclose this technical feature. Furthermore, all dependent and independent claims refering back to new claim 6 cannot be allowed for the same reason (claims 7-17).
The following examination has been carried out for the scope of the current set of claims, which does not go beyond the content of the application first filed.
New claims 1-5 seem to be allowable vis à vis Article 19(2) PCT.

V.2. Novelty:
The subject matter of claims 1-17 seems to be novel vis à vis the disclosed prior art.
V.2.1. In D1 unsubstituted copper phthalocyanine is chlorosulphonated and subsequently reacted with certain amines and ammonium compounds. Thereby also alpha-substituted compounds are synthesised, bearing up to 4 substituents in total (see D1, examples). The product of current claim 1 covers only the beta-species.
D2,D3 disclose phthalocyanine dyestuffs with complex diamino alkylene substituents; starting products here are also, as in D1, unsubstituted phthalocyanine skelletons [to unsubstituted copper resp. nickel phthalocyanines is added chlorosulphonic acid]. Beneath the beta-isomers also the alpha ones are expected as the final products.
As the starting product of the phthalocyanines in D4 Reactive Blue 25 is used. With reference to the Register File ((C) FILE REGISTRY) of the Chemical Abstracts database,

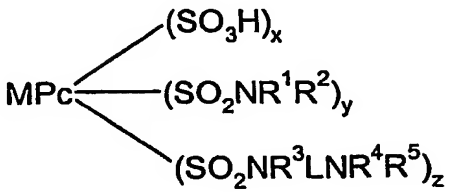
the molecular formula of the compound C.I. Reactive Blue 23 [8Cl, 9Cl; entered STN: 16 Nov 1984; other names: Levafix Brilliant Blue 4GL;Levafix Brilliant Blue I4G] is **unspecified**. D4 can therefore not considered as being explicitly novelty destroying for claim 1.
D5 starts also with the unsubstituted copper phthalocyanine which is reacted with chlorosulphonic acid (see D5, examples), so do the authors of D6 (see example 8).
Claim 1 therefore seems to be novel the prior art.

V.3. Inventive Step:
The application does not fulfill the requirements of Article 33(1) PCT, because the claims 1-17 do not involve an inventive step in the sense of Article 33(3) PCT.
V.3.1. The problem underlying the current application can be seen in 'providing ink jet inks bearing certain fastness properties, especially less fading on exposure to light or common oxidising gases such as ozone'.
D2,D3,D4 mention the problem of stabilty against ozone attacks and emphasised the improved fastness of the dyestuffs resp. inks prepared therein. This problem is, on the other hand, not related in D2-D4 to the substitution pattern of the dyes (alpha or beta positions) in discussion. In the current application it could be demonstarted that the claimed dyes, compared to a alpha/beta-substituted dye (comparitive dye 2), give a significant improvement concerning the ozone fastness. Although D2-D4 are silent about the relationship between the alpha/beta substitution pattern and the ozone fastness, it is still not clear from any comparitive test, that a 'pure beta-fraction' of the phthalocyanines gives better ozone fastness compared to a 'mixed alpha/beta-fraction'.
The dyes used in the comparison tests in the current aplication do not bear a second amino function with a N-L-N (substituents with the index 'z' in formula (1)) moiety. Especially the inks of examples 2, 6 and 7 of D4 would be very interesting to serve as comparitive candidates for the ozone test. Such a comparitive test could prove inventivity of the claimed dyes. Claim 1 (as well as claims 2-17) are therefore not be regarded as being inventive over D4.

VII. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document D4 is not mentioned in the description, nor is this document identified therein.

CLAIMS

1. A mixture of phthalocyanine dyes of Formula (1) and salts thereof:

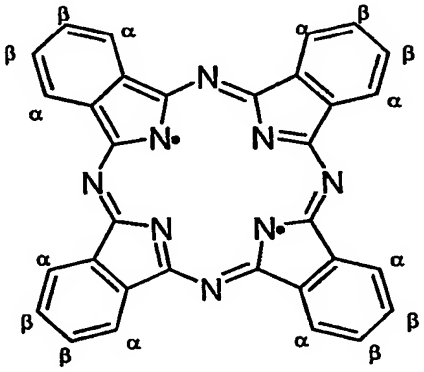


Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of formula;



L is optionally substituted C_{1-20} alkylene, alkyenylene or alkynylene, optionally interrupted by –O-, -NH- or -S-;

R^1, R^2, R^3 and R^4 independently are H or optionally substituted C_{1-4}alkyl;

R^5 is H or an optionally substituted hydrocarbyl; or

R^4 and R^5 together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

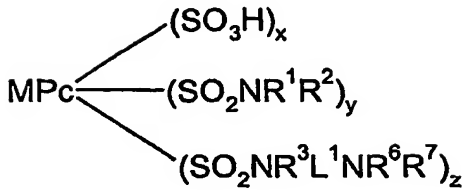
z is 0.1 to 3.8;

the sum of (x+y+z) is 4;

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring; and

the mixture of dyes of Formula (1) are obtainable by a process which comprises cyclisation of β-sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide.

2. A mixture of phthalocyanine dyes according to claim 1 of Formula (2) and salts thereof:

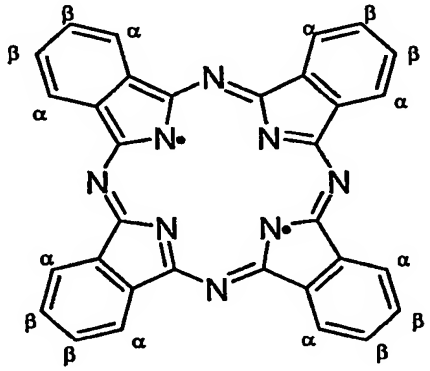


Formula (2)

wherein:

M Cu or Ni;

Pc represents a phthalocyanine nucleus of formula;



L^1 is optionally substituted C_{1-8} alkylene optionally interrupted by –O-, -NH- or -S-;

R^1, R^2, R^3 and R^6 independently are H or optionally substituted C_{1-4}alkyl;

R^7 is H, optionally substituted aryl, optionally substituted alkyl or optionally heterocyclyl; or

R^6 and R^7 together with the nitrogen atom to which they are attached represent an optionally substituted 5 or 6 membered aliphatic or aromatic ring;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

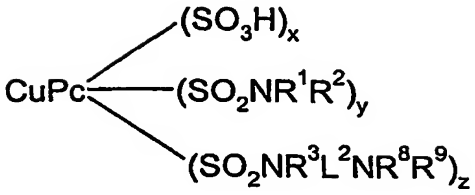
the sum of (x+y+z) is 4;

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring: and .

the mixture of dyes of Formula (2) are obtainable by a process which comprises cyclisation of β-sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide.

3. A mixture of phthalocyanine dyes according to either claim 1 or claim 2 wherein M is Cu.

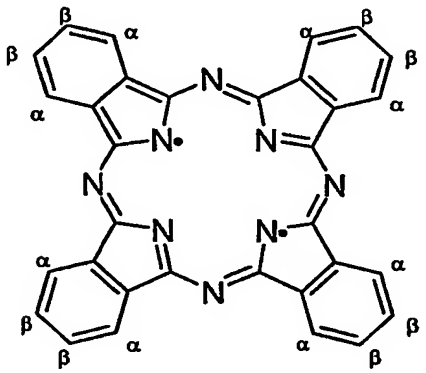
4. A mixture of phthalocyanine dyes according to any one of the preceding claims of Formula (3) and salts thereof:



Formula (3)

wherein:

Pc represents a phthalocyanine nucleus of formula;



L^2 is optionally substituted C_{1-4} alkylene;

R^1, R^2, R^3 and R^8 independently are H or methyl;

R^9 is H or phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents; or

R^8 and R^9 together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6- membered aliphatic or aromatic ring;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4;

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring; and .

the mixture of dyes of Formula (3) obtainable by a process which comprises by cyclisation of β-sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide.

5. A mixture of phthalocyanine dyes according to claim 1 obtainable by a process which comprises cyclisation of 4-sulfo-phthalic acid in the presence of a nitrogen source, a copper or nickel salt and a base.

6. A mixture of phthalocyanine dyes according to any one of the preceding claims wherein x has a value of 0.5 to 3.0, y has a value of 0.5 to 3.0 and z has a value of 0.5 to 3.0.

7. A mixture of phthalocyanine dyes according to any one of the preceding claims free from fibre reactive groups.

8. A composition comprising a mixture of phthalocyanine dyes according to any one of claims 1 to 7 and a liquid medium.

9. A composition according to claim 8 wherein the liquid media comprises a mixture of water and organic solvent or organic solvent free from water.

10. A composition according to either claim 8 or claim 9 wherein at least 70% by weight of the total amount of phthalocyanine dye is of Formula (1).

11. A composition according to claim 10 wherein at least 95% by weight of the total amount of phthalocyanine dye is of Formula (1).

12. A composition that comprises:
(a) from 0.5 to 15 parts of a mixture of phthalocyanine dyes according to any one of claims 1 to 7; and
(b) from 99.5 to 85 parts of a liquid medium;
wherein all parts are by weight.

13. A composition according to claim 12 that comprises:
(c) from 1 to 5 parts of a mixture of phthalocyanine dyes according to any one of claims 1 to 7; and
(d) from 99 to 95 parts of a liquid medium;
wherein all parts are by weight.

14. A composition according to any one of claims 8 to 13 which is an ink suitable for use in an ink jet printer.

15. A process for forming an image on a substrate comprising applying an ink according to claim 14 thereto by means of an ink-jet printer.

16. A material printed with a composition according to any one of claims 8 to 14 or a mixture of phthalocyanine dyes as described in any one of claims 1 to 7 or by a process according to claim 15.

17. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in claim 14.